Large negative linear compressibility of $\text{Ag}_3[\text{Co}(\text{CN})_6]$

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Silver(I) hexacyanocobaltate(III), $\text{Ag}_3[\text{Co}(\text{CN})_6]$, shows a large negative linear compressibility (NLC, linear expansion under hydrostatic pressure) at ambient temperature at all pressures up to our experimental limit of 7.65(2) GPa. This behavior is qualitatively unaffected by a transition at 0.19 GPa to a new phase $\text{Ag}_3[\text{Co}(\text{CN})_6]$ -II, whose structure is reported here. The high-pressure phase also shows anisotropic thermal expansion with large uniaxial negative thermal expansion (NTE, expansion on cooling). In both phases, the NLC/NTE effect arises as the rapid compression/contraction of layers of silver atoms—weakly bound via argentophilic interactions—is translated via flexing of the covalent network lattice into an expansion along a perpendicular direction. It is proposed that framework materials that contract along a specific direction on heating while expanding macroscopically will, in general, also expand along the same direction under hydrostatic pressure while contracting macroscopically.

negative linear compression | negative thermal expansion | high-pressure | framework materials | flexibility

Negative linear compressibility (NLC), whereby a material expands along a specific direction on increasing hydrostatic pressure, is a very unusual effect. Indeed in a study of elastic constant data from 500 noncubic crystal phases, only 13 displayed NLC, and of those, 11 structures were of monoclinic or lower symmetry (1). Despite its rarity, NLC is a highly attractive mechanical property, with a key application being the development of effectively incompressible optical materials (1, 2). Such materials could be used in high-pressure environments, such as in optical telecommunications devices that must function at deep-sea pressures >1,000 atm. NLC also offers a means of producing ultrasensitive pressure detectors, such as interferometric optical sensors for sonar and aircraft altitude measurements. The effect is also often coupled to so-called “auxetic” behavior, which is itself being used to improve shock resistance in, e.g., body armor (3).

Of the few known examples among inorganic materials, the most pronounced NLC effects have been reported for LaNbO_4 (4), elemental Se (5), the BXO_4 ($X = \text{P}, \text{As}$) family (6), and the spin-Peierls compound α' - NaV_2O_5 (7). In some other cases, transient NLC behavior may occur only at pressures just above a strain-induced phase transition to a structure of lower symmetry (e.g., refs. 8 and 9), or as a result of an uptake of additional interstitial molecules (10, 11).

One fundamental barrier to the practical application of NLC is that its magnitude is generally much smaller than the “normal” (positive) compressibilities of standard materials.* By convention, linear compressibility is defined as the relative rate at which a given dimension ℓ decreases with pressure (at constant temperature): $K_\ell = -(\partial \ln \ell / \partial p)_T$. Typical values for crystalline materials lie in the range $K_\ell \approx 5\text{--}20 \text{ TPa}^{-1}$ (12) (i.e., their linear dimensions decrease by $\approx 1\%$ for each GPa increase in pressure). In contrast, a NLC coefficient $K_c \approx -2 \text{ TPa}^{-1}$ has been reported for α -cristobalite structured BaSO_4 (6); in trigonal Se, one finds $K_c \approx -1.2 \text{ TPa}^{-1}$ (5), whereas in monoclinic LaNbO_4 , NLC appears either to be negligible [$K_{[210]} \approx -0.2 \text{ TPa}^{-1}$ (4)] or similar to that in Se (13).

Fig. 1. Compression mechanism in $\text{Ag}_3[\text{Co}(\text{CN})_6]$, exaggerated for illustrative purposes: In order for the framework to reduce its volume (either in response to a decrease in temperature or an increase in pressure), it must expand along the trigonal axis (c).

Here, we use high-pressure neutron powder diffraction to show that substantially stronger NLC behavior is to be found in the framework material $\text{Ag}_3[\text{Co}(\text{CN})_6]$, for which we obtain $K_c \approx -75 \text{ TPa}^{-1}$. The structural changes are so rapid that a first-order transition is found to occur at 0.19 GPa to a previously unidentified phase, whose structure is 16% more dense. Remarkably, this new phase also shows a strong NLC effect, with $K_c \approx -5 \text{ TPa}^{-1}$ up to our experimental limit of 7.65 GPa. We chose to study $\text{Ag}_3[\text{Co}(\text{CN})_6]$ because, upon heating, its framework structure contracts remarkably strongly along 1 direction as the overall volume increases (14). Should the same geometric mechanism operate under changes in pressure, we reasoned that, by flexing to reduce its volume, the lattice would be forced to expand along the negative thermal expansion (NTE) axis (Fig. 1). Moreover, because NTE is so strong in this material (its linear coefficients of thermal expansion, $\alpha \approx \pm 130 \text{ MK}^{-1}$, are ≈ 10 times larger than those of typical materials), we expected the magnitude of any NLC effect to be similarly pronounced.

The concept of looking for unusual pressure-dependent behavior in NTE materials has a sound physical basis. These materials often have low-density structures and, importantly,

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*The reporting of NLC is often done on the basis of fitting $\Delta \ell(p)/\ell_0$ to a polynomial function $A p + B p^2 + C p^3 + \dots$ and then quoting the value of A as $K_{\ell 0}$. This will tend to overestimate $K_{\ell 0}$ in cases where NLC diverges at low pressures. We have chosen to fit $\Delta \ell(p)$ either to a straight line or to an empirical equation of the form $\lambda(p - p_c)^\nu$ and hence to extract $K(p)$; we quote representative compressibilities from these functions. The values quoted here for Se are less extreme than those published (5) but are actually more representative of the overall behavior. Likewise, our analysis of published LaNbO_4 data gives a less negative compressibility (and a slightly different orientation for the corresponding principal axis: $\approx [210]$) (4).

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possess phonon modes with negative Grüneisen parameters (i.e., some vibrational energies decrease under applied pressure). By way of an example, the isotropic NTE material ZrW_2O_8 exhibits both a low-pressure phase transition (15) and pressure-induced amorphization (16), the latter attributed to increased bonding as the energies of many rigid unit modes fall to zero (17). Another NTE material, $\text{Zn}(\text{CN})_2$, actually becomes softer at higher pressures, reflecting an anomalous decrease in vibrational energies driven by changes to the underlying potential surface (18). Furthermore, in elemental Se the mechanism responsible for NTE along the Se spiral axis (19) probably accounts for NLC along the same direction (5); indeed the concept of a more general link between NTE and NLC is developed as part of the present study.

We begin by reporting the compressibility of the ambient phase $\text{Ag}_3[\text{Co}(\text{CN})_6]\text{-I}$. We then report the structure of the previously undescribed high-pressure phase formed at 0.19 GPa, followed by a description of its pressure- and temperature-dependent behavior. We conclude with a discussion concerning the general relationship between NTE and NLC in framework materials.

Results and Discussion

Compressibility of Ambient Pressure Phase I. The structure of $\text{Ag}_3[\text{Co}(\text{CN})_6]\text{-I}$ consists of 3 interpenetrating distorted cubic networks, each with CoC_6 octahedra at the cube apices and with edges formed by approximately linear —CN—Ag—NC— bridges (20). This topology gives rise to a trigonal structure (in space group $P\bar{3}1m$) in which layers of CoC_6 octahedra alternate with layers of Ag atoms, stacked parallel to the crystal c axis at intervals of $c/2$ (Fig. 1). Within individual layers, the $[\text{Co}(\text{CN})_6]$ octahedra are arranged on a triangular lattice, and their separation corresponds directly to the lattice parameter a . The Ag atoms, which are separated by the distance $a/2$, are arranged on a related Kagome lattice. These layers are connected via flexible Co—CN—Ag—NC—Co covalent linkages, oriented approximately parallel to the (101) directions. This particular arrangement means the covalent bonding interactions do not determine the absolute crystal dimensions but act only to couple any expansion within the (001) plane to a contraction along c (and vice versa). Instead, the lattice dimensions appear to reflect the equilibrium separation of weak dispersion-like Ag–Ag “argenophilic” interactions (21). Indeed, the crystal thermal expansion resembles that of van der Waals solids (e.g., Xe) more strongly than typical framework materials (14).

We collected neutron diffraction patterns for $\text{Ag}_3[\text{Co}(\text{CN})_6]\text{-I}$ at 3 pressure values before the material transformed into a new phase at a transition pressure of 0.19 GPa. We discuss this transition in more detail below but consider first the compressibility of the ambient phase, for which lattice parameters are shown in Fig. 2. We see in Fig. 2A that trigonal $\text{Ag}_3[\text{Co}(\text{CN})_6]\text{-I}$ does indeed show NLC with a significant expansion along the c axis as pressure increases. This is accompanied by an even larger contraction along a . Numerical values for the compressibilities were obtained by linear fits to the data, giving $K_a = +115(8)$ TPa^{-1} and $K_c = -76(9)$ TPa^{-1} . This NLC effect along c is more than an order of magnitude greater than that observed in (e.g.) BaSO_4 (6). Indeed, we believe that $\text{Ag}_3[\text{Co}(\text{CN})_6]\text{-I}$ exhibits the strongest NLC effect yet reported for any inorganic material. We note also that the compressibility along a is also remarkable for its magnitude and similar to that of solid Xe, for which $K_a = +130(12)$ TPa^{-1} at 100 K (22).

Considering, in turn, the effect of pressure on unit cell volume, we calculate a bulk modulus of $B = 6.5(3)$ GPa from a linear fit to the data in Fig. 2C. We note that this value is small, and not dissimilar to the estimate $B_{\text{calc}} = 9.9$ GPa obtained by using ab initio calculations (23). Unfortunately, the paucity of data does

Fig. 2. Pressure dependence of various structural parameters: lattice parameters (A), linear compressibilities extracted from parameterized fits to the lattice parameter data (B), and volume per formula unit V/Z (C). The *Inset* in C shows linear (Phase I) and third-order Birch–Murnaghan (Phase II) fits to the V/Z data near the phase transition.

not allow us to determine the pressure derivative B' with any certainty.

Phase Transition and Structure of Phase II. Further compression precipitates a transition at 0.19 GPa to a new phase, $\text{Ag}_3[\text{Co}(\text{CN})_6]\text{-II}$, accompanied by a volume change $\Delta V/V = 16.25(4)\%$ that is much larger than that observed over the whole temperature range at ambient pressure (14). This volume change includes compression in all directions, but the compression is

Fig. 3. Representations of the pressure-induced structural transition in $\text{Ag}_3[\text{Co}(\text{CN})_6]$. (A) In both the ambient trigonal phase I (Left; shown with the outline of its monoclinic supercell for ease of comparison) and high-pressure monoclinic phase II (Center and Right), $[\text{Co}(\text{CN})_6]$ octahedra (shown in polyhedral representation) are connected via Ag atoms (large spheres). (B) The framework topology differs between phases because the shear parallel to a/a_{II} is coupled to a shift of $2/3$ of the Ag atoms by $1/4$ of a unit cell in the same direction. This transforms the argentophilic Kagome layers of phase I into a reentrant honeycomb ("bow-tie") arrangement in phase II. (C) Subsequent compression increases the extent of "puckering" in this 2-dimensional lattice, approaching a triangular network.

most significant along a direction parallel to the c axis of phase I, with a relative change in length of $\Delta\ell/\ell = 10.78(9)\%$ compared with values of between $3.01(3)\%$ and $3.21(3)\%$ for the basal plane directions.

The $\text{Ag}_3[\text{Co}(\text{CN})_6]$ -II diffraction patterns could be indexed according to a unit cell in the monoclinic space group $C2/m$, a maximal subgroup of $P31m$. These 2 groups are related by loss of the threefold inversion axis in $P31m$, and give $a_{\text{II}} \approx a_{\text{I}}$, $b_{\text{II}} \approx \sqrt{3}b_{\text{I}}$, and $c_{\text{II}} \approx c_{\text{I}}$ (where II and I refer to monoclinic phase II and trigonal ambient pressure phase I, respectively; see Fig. 3A). The absence of a $\bar{3}$ axis parallel to c allows a shear of the unit cell along a perpendicular direction (parallel to a_{II}); the extent of this shear is related to the monoclinic angle β_{II} , which we found to be $\approx 100^\circ$ over the pressure range studied ($90^\circ = \text{no shear}$). Unit cell dimensions at the low- and high-pressure extremes of our data were as follows ($Z = 2$ in both cases): $[0.226(10) \text{ GPa}] a = 6.6934(13) \text{ \AA}$, $b = 11.5391(18) \text{ \AA}$, $c = 6.5661(13) \text{ \AA}$, $\beta = 101.479(13)^\circ$, $V = 496.99(9) \text{ \AA}^3$; $[7.65(17) \text{ GPa}] a = 5.8657(23) \text{ \AA}$, $b = 10.270(3) \text{ \AA}$, $c = 6.908(3) \text{ \AA}$, $\beta = 103.079(29)^\circ$, $V = 405.36(19) \text{ \AA}^3$.

Our first structural model for this phase simply incorporated a shear into the network connectivity of phase I. One-third of the approximately linear $\text{Co}-\text{CN}-\text{Ag}-\text{NC}-\text{Co}$ linkages of phase I (those roughly parallel to $[101]_{\text{II}}$, and whose central Ag atom we denote by Ag1) are then stretched taut, whereas the other $2/3$ (now distinct by symmetry, with central atoms Ag2) are very strongly buckled. Structural refinement against our data at $0.23(2) \text{ GPa}$ produced acceptable fits with this model, but gave very short Ag2—N bond lengths of $1.81 \text{ \AA}$ within the "buckled" $\text{Co}-\text{CN}-\text{Ag2}-\text{NC}-\text{Co}$ chains (note an Ag—N distance of $2.02 \text{ \AA}$ in phase I). In addition, it was not possible to refine sensible atomic displacement parameters for the Ag2 atoms [located in this model at $(\frac{1}{4}, \frac{1}{4}, \frac{1}{2})$]. Instead, from among a number of different ordered and disordered models, our data showed a preference for the Ag2 atom to be located at $(0, y, \frac{1}{2})$ with $y \approx \frac{1}{4}$. This model gave a good fit to the data [see supporting information (SI)], produced a stable refinement and gave sensible atom positions, $[\text{Co}(\text{CN})_6]$ octahedral geometries, bond

lengths, and thermal displacement parameters; refined atom coordinates and isotropic displacement parameters are given in Table 1, and the model itself is illustrated in Fig. 3A.

The Ag2 shift of $\approx \frac{1}{4}a_{\text{II}}$ converts the argentophilic Kagome lattice into a "reentrant honeycomb" or "bow-tie" arrangement (Fig. 3B and C). An important consequence is that the original

Table 1. Refined atomic coordinates and isotropic displacement parameters for $\text{Ag}_3[\text{Co}(\text{CN})_6]$ -II from data measured at $0.226(10) \text{ GPa}$

Atom	x	y	z	$B_{\text{iso}}, \text{ \AA}^2$
Co	0	0	0	0.4(7)
	0	0	0	0.65(10)
Ag1	0.5	0	0.5	4.4(8)
	0.5	0	0.5	0.65(10)
C1	0.8252(22)	0	0.1818(21)	0.24(19)
	0.842(6)	0	0.201(4)	0.65(10)
N1	0.7150(17)	0	0.3020(17)	0.74(18)
	0.757(4)	0	0.3306(28)	0.65(10)
Ag2	0	0.2404(13)	0.5	2.1(3)
	0	0.1904(28)	0.5	0.65(10)
C2	0.1634(17)	0.1190(8)	0.1574(15)	1.15(17)
	0.2108(29)	0.1227(15)	0.1448(29)	0.65(10)
N2	0.2582(14)	0.1854(6)	0.2592(19)	1.13(13)
	0.324(3)	0.1984(13)	0.2415(22)	0.65(10)

Corresponding values at $7.65(17) \text{ GPa}$ are shown in italics. For the higher-pressure data, thermal displacements were modeled by using a common parameter, whereas the low-pressure data were of sufficient quality to allow refinement of individual displacement parameters.

Co—CN—Ag₂—NC—Co linkages, which connect Co atoms of neighboring (010)_I planes in phase I, are replaced by bent linkages that join Co atoms of the same (010)_{II} plane in phase II. This means that there is actually no covalent connectivity between adjacent (010) planes in the high-pressure structure. Instead, neighboring planes “interdigitate” as the —CN—Ag₂—NC— “hoops” of each layer project into cavities of the next (see Fig. 3*A Upper Center*). Consequently, one might expect the structure to be reasonably soft along the *b*_{II} axis because the interlayer separation will be dictated primarily by weak Ag—Ag interactions.

We note that, in principle, the Ag₂ displacements need not be coupled to the shear; that the 2 events occur simultaneously suggests that Ag—Ag interactions may help drive the transition. Intriguingly, the lattice parameters of phase I just below *p*_c are significantly less extreme than those obtained by cooling at ambient pressure, and so the material would be capable of further volume reduction in this phase than that observed under increasing pressure. We considered the possibility that phase I may be a metastable form, but we found that the phase was quantitatively recoverable upon pressure release. The extent of Ag displacements is strongly temperature dependent, and it may be that thermal motion of the Ag atoms encourages a transition at a greater volume than that obtainable upon cooling. We note also the multipolar interactions between neighboring Ag atoms will be frustrated in the Kagome layers of phase I, but this frustration will be ameliorated in the bow-tie network of phase II. Whether frustration plays an additional role in the thermodynamics of this compound is an interesting possibility that we leave as an open question for further study.

Compressibility of High-Pressure Phase II and Pressure-Dependent Changes to Structure. The decrease from trigonal to monoclinic symmetry complicates the compressibility behavior of Ag₃[Co(CN)₆]-II. The *a*_{II} and *c*_{II} axes are no longer principal axes, but in practice, we find that the principal axes [in the (010) plane] coincide with the unit cell axes to within 5°. So the values *K*_{*a*_{II}}, *K*_{*b*_{II}}, and *K*_{*c*_{II}} give quite good approximations to the principal components of the compressibility tensor. The related parameter *K*_{*c*_{II}} sin β_{II} corresponds to the compressibility perpendicular to Ag- and [Co(CN)₆]-containing layers.

We refined values of the phase II lattice parameters at 15 points over the pressure range 0.19–7.65 GPa; our results are shown in Fig. 2*A*, and the corresponding lattice parameter values and fits to data are given in SI. What is immediately clear is that Ag₃[Co(CN)₆]-II also shows NLC, because the terms *c*_{II} and *c*_{II} sin β_{II} increase with increasing pressure. The lattice parameter variation was fitted according to a set of empirical expressions $x(p) = x_0 + \lambda(p - p_c)^n$, where in this case, *p*_c = 0.19 GPa. This enabled calculation of a smooth compressibility curve for each direction in the lattice; the corresponding *K* values are shown in Fig. 2*B*. Although values approach those of phase I just above the phase transition, average values from linear fits to lattice parameter data >3 GPa give principal components of the compressibility tensor of +15.2(9), +9.6(5), and −5.3(3) TPa^{−1} along axes approximately parallel to *a*, exactly parallel to *b*, and approximately parallel to *c*, respectively. Although NLC is much less extreme in this phase than in phase I, the behavior is still significantly stronger than that observed in all previous studies. The pressure dependence of the unit-cell volume for this phase can be fitted well by a third-order Birch–Murnaghan equation of state (24), giving *B*_{*p*_c} = 11.8(7) GPa and *B*' = 13.5(12) (Fig. 2*C*). These values show that phase II is also initially very soft but becomes significantly harder with increasing pressure (i.e., *B*' ≫ 4). A second-order Birch–Murnaghan fit, for which *B*' is constrained to equal 4, gives a substantially lower *R*² value (0.9705 vs. 0.9987) and clearly does not represent the data well (see Fig. 2*C Inset*). Consequently, Ag₃[Co(CN)₆]-II shows very strong

third-order behavior, of a degree normally found only for low-dimensional materials, e.g., graphite-like BC (*B*' = 8.0) (25) and layered GeSe₂ (*B*' = 9.1) (26)]. Such a large value of *B*' in a fully 3-dimensional framework suggests that the elastic constants exhibit anomalous pressure dependencies, a finding that we hope will stimulate further investigation elsewhere.

So how does the structure itself vary under pressure? We found that the [CoC₆] coordination geometries were essentially unaffected by lattice compression and that the original connectivity of this phase was maintained throughout the entire pressure range (see Table 1 for atom coordinates at 2 representative pressure values). Where the variation is most noticeable is in the magnitude of the “interdigitation” effect described above. This can be quantified by the Ag₂*y* coordinate, which decreases from an initial value of 0.2404(13) at 0.226(10) GPa to 0.1904(28) at 7.65(17) GPa as the extent of interdigitation increases. This has very little effect on any covalent bonding interactions in the framework, but it does vary the geometry of Ag—Ag interactions in the Ag-containing layers: The “knot” of the bow-tie lattice is increasingly “pinched” as *y*_{Ag₂} becomes progressively smaller than $\frac{1}{4}$ (Fig. 3*C*). As a result, all Ag...Ag neighbor distances become more similar with increasing pressure, with the overall arrangement approaching that of a triangular lattice (which would occur for *y*_{Ag₂} = $\frac{1}{6}$) but would not increase the lattice symmetry). We believe the mechanism responsible for NLC to be strongly related to this change in Ag environment. The [Co(CN)₆] octahedra sit above and below the knots of the Ag-containing bow-tie lattice; as these knots tighten, the octahedra are forced to move in a direction perpendicular to the Ag sheets, resulting in the corresponding lattice parameter increase. The relatively large positional changes involved are permitted by the flexibility of the lattice: both in terms of the weak argentophilic forces between neighboring (010)_{II} layers and in terms of the geometric underconstraint of Co—CN—Ag linkages.

We note in passing that the reentrant honeycomb lattice is an example of a 2-dimensional structure with a negative Poisson's ratio (27, 28). Such materials (also known as auxetics) have important mechanical properties; see, for example, refs. 3 and 29 and references therein. In the present context, we note that this property is responsible for coupling the compressibility along *b* to behavior of a similar sign and magnitude along *a*.

Thermal Expansion of Phase II. Our original motivation for studying NLC in Ag₃[Co(CN)₆] was that—although thermodynamics allows for different compression mechanisms under pressure increase and temperature reduction—we reasoned that NLC and NTE may be linked in many cases. Having found both effects to occur in phase I, we were interested to determine whether phase II also shows NTE.

The temperature dependence of the lattice constants, measured at an applied pressure of 0.395(10) GPa, is illustrated in Fig. 4*A*. Again, the coefficients of thermal expansion α_{*a*} and α_{*c*} need not correspond to principal components of the thermal expansion tensor, but in practice, we find that there is little difference between the two. What is obvious from our measurements is that Ag₃[Co(CN)₆]-II shows large PTE along *a* and *b*, but there is a similarly strong NTE effect along *c*. From linear fits to the data, we obtain principal thermal expansivities of α = +13.3(25), +30.0(16) and −23(3) MK^{−1} along axes approximately parallel to *a*, exactly parallel to *b*, and approximately parallel to *c*, respectively; the volume coefficient of thermal expansion is α_V = +20.5(25) MK^{−1}. The NTE effect approximately parallel to *c* is approximately twice that of ZrW₂O₈ at ambient pressure (30) and comparable with that in other cyanides such as Zn(CN)₂ and Cd(CN)₂ (31). It is also 6–7 times smaller than in phase I; so, perhaps fortuitously, both the compressibilities and the thermal expansivities of the 2 phases

NLC in $\text{Ag}_3[\text{Co}(\text{CN})_6]$, an effect that is many times larger even than the typical (positive) compressibilities of “normal” solids. We have discovered and characterized its trigonal–monoclinic phase transition at 0.19 GPa, and have shown that the high-pressure form also exhibits both NLC and NTE. The second key outcome is to show that Grüneisen isotropy allows a more general expectation that anisotropic NTE framework materials will also show NLC (and vice versa). Thermal expansion is more readily measured than compressibility, presenting a useful method for screening likely NLC candidates.

Materials and Methods

The polycrystalline $\text{Ag}_3[\text{Co}(\text{CN})_6]$ sample was prepared as in ref. 14 and loaded into either a TiZr helium-gas pressure cell mounted on a closed cycle helium refrigerator ($0 < p < 0.6$ GPa, $20 < T < 300$ K, sample volume ≈ 1.5 cm³) or an encapsulated TiZr gasket arrangement within a Paris–Edinburgh (P–E) press ($0 < p < 9$ GPa, sample volume ≈ 90 mm³) (39). TiZr, alloyed in the correct proportions, has an average neutron scattering length of zero and so does not produce background Bragg scattering. Included in the sample space within the gasket of the P–E press was a lead sphere, for use as a pressure marker, and

a deuterated methanol–ethanol mixture, as a pressure transmitting fluid. Sample pressures in the gas pressure cell were determined directly from the He pressure (variance, $dp \approx 100$ bar, 0.01 GPa); those in the P–E press were obtained by fitting the measured Pb lattice parameter to the known equation of state for Pb (as described in ref. 40; $dp \approx 0.15$ – 0.2 GPa). Data were collected as a function of neutron time-of-flight at the ISIS Spallation Neutron Source, Rutherford Appleton Laboratory, U.K. by using the Polaris (41) and Pearl (42, 43) diffractometers for measurements within the gas cell and P–E press, respectively. Typical data collection times were ≈ 4 hours per pressure. Standard routines were used for data focusing and normalization and to account for pressure cell absorption. The resulting normalized powder diffraction patterns were then analyzed by using the GSAS Rietveld refinement package (44) using data from detectors centered around $2\theta = 35^\circ$ and $2\theta = 90^\circ$ (Polaris) or $2\theta = 90^\circ$ only (Pearl), the latter a multiphase refinement including the sample, Pb (pressure marker) and weak contributions from Ni and WC (anvil components).

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